

Taco Complex Templated Syntheses of a Cryptand/Paraquat [2]Rotaxane and a [2]Catenane by Olefin Metathesis

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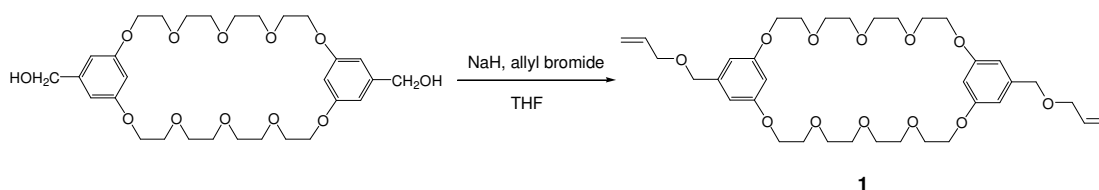
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1. Materials and Methods

BMP32C10-diol^{S1} was synthesized according to a literature procedure. Grubbs' II catalyst was purchased from Aldrich. Allyl bromide and NaH were purchased from Alfa Aesar. Solvents were either employed as purchased or dried according to procedures described in the literature. ¹H NMR spectra were collected on a temperature-controlled either 400 MHz or 500 MHz spectrometer. Electrospray ionization mass spectra were obtained on a Bruker Esquire 3000 Plus spectrometer. High-resolution mass spectrometry experiments were performed on a Bruker Daltonics Apex III spectrometer. X-ray diffraction was carried out on a Bruker Smart Apex II.

2. Synthesis and characterization of BMP32C10 derivative 1



NaH (0.144 g, 6.00 mmol) was added to a 150 mL round-bottomed flask and then THF (30 mL) was added under nitrogen atmosphere. After the mixture was cooled to 0 °C, a solution of BMP32C10-diol (1.19 g, 2.00 mmol) in THF (50 mL) was added dropwise over 1 h. The mixture was stirred for further 30 min and a solution of allyl bromide (0.532 g, 4.40 mmol) in THF (30 mL) was added dropwise during 1 h. After it was stirred for further 12 h at room temperature, the reaction was quenched with MeOH/H₂O. The solvent was evaporated *in vacuo* and the residue partitioned between CH₂Cl₂ (100 mL) and water (50 mL). The organic layer was dried with anhydrous Na₂SO₄ and evaporated *in vacuo* to give a residue, which was purified by column chromatography (SiO₂: EtOAc/petroleum ether = 2:1) to afford **1** (1.160 g, 86%) as a white solid, mp 63–64 °C. ¹H NMR (400 MHz, CDCl₃, 22 °C) δ (ppm): 6.49 (4 H, s), 6.40 (2 H, d, J = 1.6 Hz), 5.98–5.88 (2 H, m), 5.31–5.17 (4 H, m), 4.42 (4 H, s), 4.07

(8 H, t, $J = 4.4$ Hz), 3.99–3.98 (4 H, m), 3.83 (8 H, t, $J = 4.4$ Hz), and 3.70–3.69 (16 H, m). Low-resolution ESI-MS: m/z 699.3 (100%) [**1** + Na]⁺.

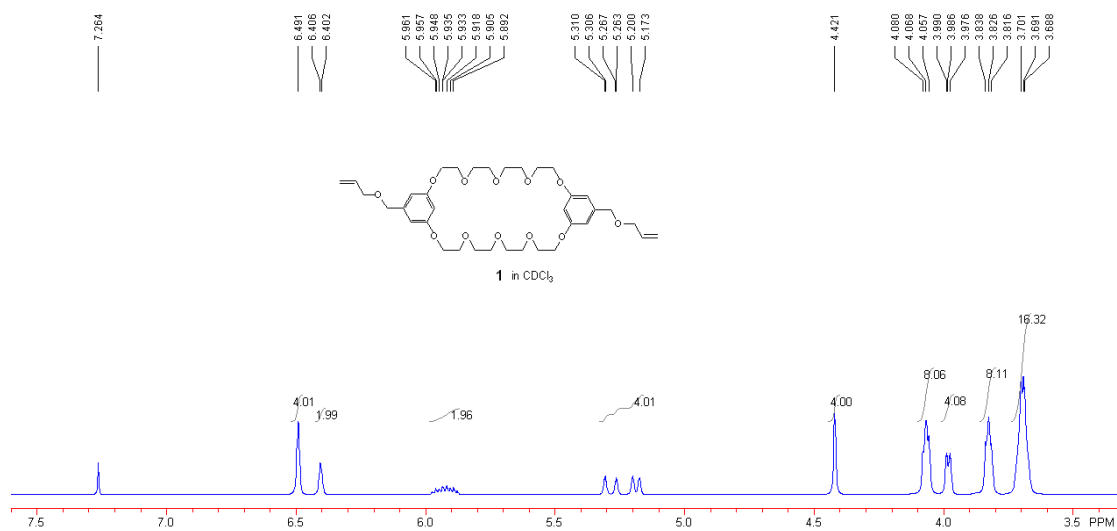


Figure S1. ¹H NMR spectrum (400 MHz, CDCl₃, 22 °C) of BMP32C10 derivative **1**.

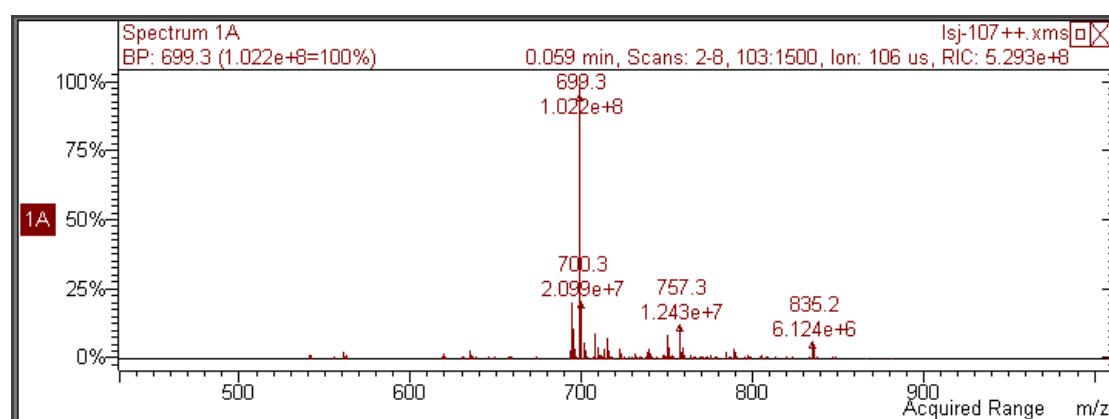
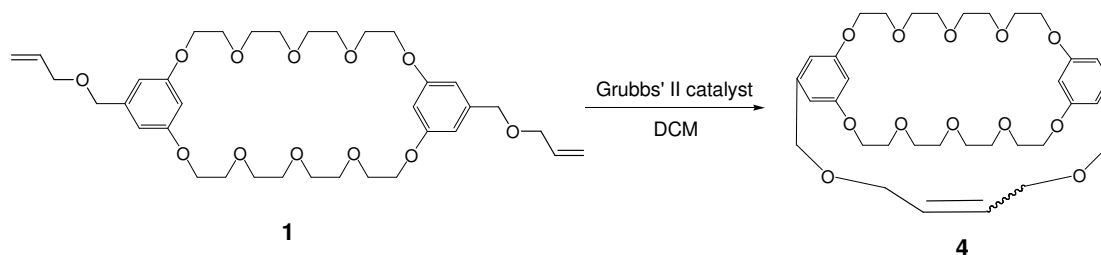


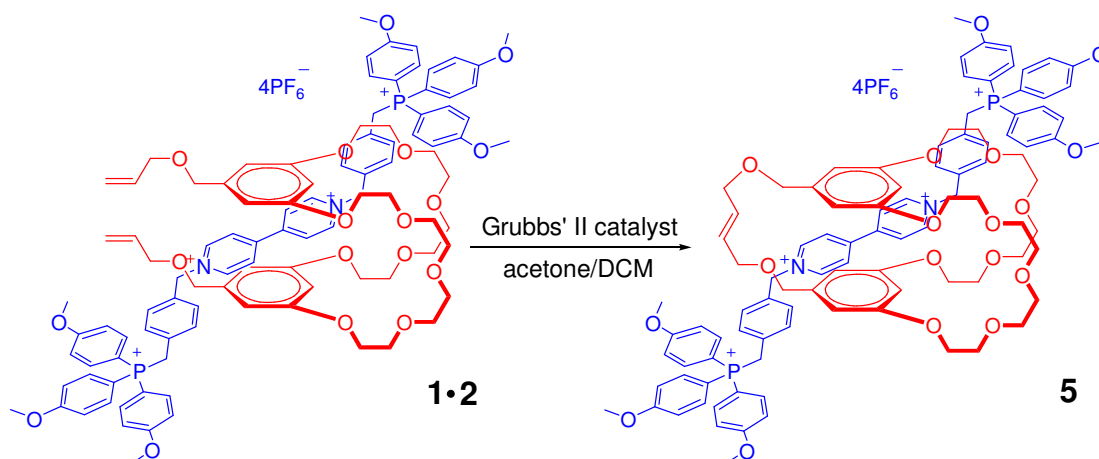
Figure S2. Low-resolution ESI-MS spectrum of BMP32C10 derivative **1**.

3. Synthesis and characterization of cryptand **4**



BMP32C10 derivative **1** (0.440 g, 0.624 mmol) was dissolved in DCM (1000 mL). Then a solution of Grubbs' II catalyst in DCM (50 mL) was syringed in over 24 h under nitrogen atmosphere. The mixture was then stirred for 72 h at room temperature. After the reaction mixture was concentrated under reduced pressure, the residue was purified by flash column chromatography (SiO₂: EtOAc/petroleum ether = 2:1) to afford cryptand **4** (350 mg, 87%) as a colorless oil. ¹H NMR (500 MHz, CD₃COCD₃, 22 °C) δ (ppm): 6.42 (3 H, d, J = 2.5 Hz, H_c of *cis*-isomer), 6.35 (1 H, d, J = 2.5 Hz, H_c of *trans*-isomer), 6.31 (2 H, t, J = 2.0 Hz, H_d), 5.71–5.69 (0.5 H, t, J = 3.5 Hz, H_a of *trans*-isomer), 5.68–5.67 (1.5 H, q, J = 2.5, 1.5 Hz, H_a of *cis*-isomer), 4.32 (1 H, s, H_b of *trans*-isomer), 4.29 (3 H, s, H_b of *cis*-isomer), 4.02–3.89 (12 H, m), 3.80–3.74 (8 H, m), and 3.64–3.57 (16 H, m). ¹³C NMR (125 MHz, CD₃COCD₃, 22 °C) δ (ppm): 160.1 (*trans*-isomer), 160.0 (*cis*-isomer), 141.6 (*cis*-isomer), 140.7 (*trans*-isomer), 129.8 (*cis*-isomer), 129.4 (*trans*-isomer), 106.1 (*cis*-isomer), 105.8 (*trans*-isomer), 100.4 (*trans*-isomer), 100.2 (*cis*-isomer), 71.5 (*cis*-isomer), 71.4 (*trans*-isomer), 70.7 (*trans*-isomer), 70.6 (*cis*-isomer), 70.4 (*cis*- and *trans*- isomer), 70.0 (*cis*-isomer), 69.5 (*cis*- and *trans*- isomer), 67.5 (*trans*-isomer), 67.5 (*cis*-isomer), and 64.7 (*trans*-isomer). Low-resolution ESI-MS: m/z 671.3 (100%) [**4** + Na]⁺.

4. Synthesis and characterization of [2]rotaxane **5**



BMP32C10 derivative **1** (13.8 mg, 0.0200 mmol) and the dumbbell-shaped paraquat derivative **2** (32.9 mg, 0.0200 mmol) was dissolved in acetone (5 mL) under nitrogen atmosphere. Then a solution of Grubbs' II catalyst (2.00 mg) in DCM (1 mL) was added at room temperature. The mixture was then stirred for 24 h. The solvent was evaporated *in vacuo* and the residue was purified by column chromatography (SiO₂: MeOH/NH₄Cl (2 M)/MeNO₂ = 17:2:1) to afford [2]rotaxane **5** (41.3 mg, 90%) as a yellow solid, mp 65–66 °C. ¹H NMR (500 MHz, CD₃CN, 22 °C) δ (ppm): 8.98 (4 H, d, J = 7.0 Hz), 7.92 (4 H, d, J = 7.0 Hz), 7.53 (4 H, d, J = 8.0 Hz), 7.46–7.41 (12 H, m), 7.16–7.12 (16 H, m), 6.30–6.29 (2 H, m), 5.89 (2 H, s), 5.86 (4 H, s), 5.24 (4 H, d, J = 3.0 Hz), 4.54 (4 H, d, J = 14.5 Hz), 3.91 (4 H, s), 3.84 (18 H, s), 3.78–3.68 (12 H, m), 3.64–3.56 (20 H, m), and 3.34–3.31 (4 H, m). ¹³C NMR (125 MHz, CD₃CN, 22 °C) δ (ppm): 165.9, 160.0, 146.6, 146.4, 141.2, 137.0 (J_{PC} = 11.4 Hz), 134.8, 133.8, 132.9 (J_{PC} = 5.2 Hz), 130.8, 126.6, 116.8 (J_{PC} = 13.8 Hz), 109.5, 108.7, 108.5, 99.3, 72.9, 72.0, 71.3 (J_{PC} = 9.8 Hz), 70.6, 70.3, 68.6, 64.4, 56.7, and 31.5 (J_{PC} = 51.6 Hz). Low-resolution ESI-MS: m/z 2320.0 (6%) [**5** + Na]⁺, 2151.2 (15%) [**5** – PF₆]⁺, 1004.0 (100%) [**5** – 2PF₆]²⁺, 931.0 (30%) [**5** – 2PF₆ – HPF₆]²⁺, 757.4 (18%) [**5** – OCH₃ – CH₃ + H₃O]³⁺, 700.4 (12%) [**5** – PF₆ – 2OCH₃ – CH₃ + Na]³⁺, 611.5 (8%) [**5** – 3PF₆ – OCH₃ – CH₃ + H₃O]³⁺, and 455.3 (38%) [**5** – 3PF₆ – 2OCH₃ + Na]⁴⁺. High-resolution ESI-MS: m/z calcd for [**5** – 2PF₆]²⁺ C₁₀₂H₁₁₄F₁₂N₂O₁₈P₄, 1003.8430, found 1003.8343,

error -8.7 ppm; and calcd for $[\mathbf{5} - 3\text{PF}_6]^{3+}$ $\text{C}_{102}\text{H}_{114}\text{F}_6\text{N}_2\text{O}_{18}\text{P}_3$, 620.9072 , found 620.9048 , error -3.9 ppm.

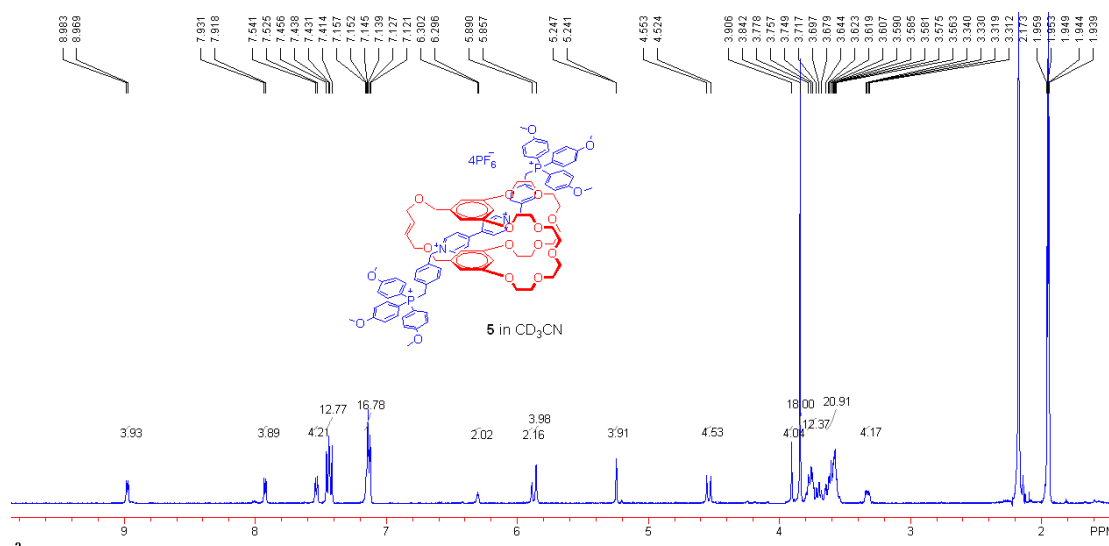


Figure S6. ^1H NMR spectrum (500 MHz, CD_3CN , 22 °C) of rotaxane **5**.

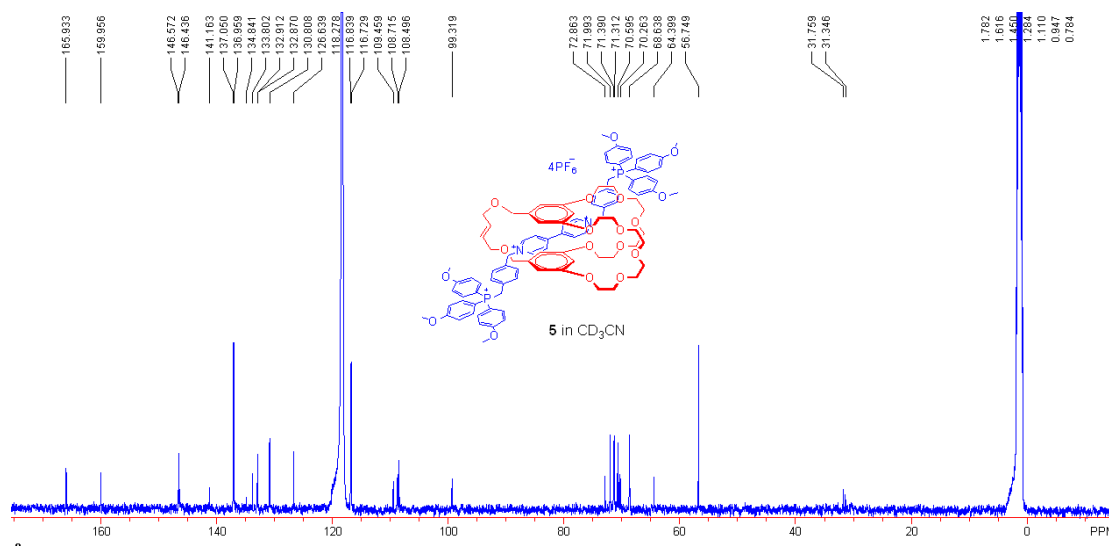


Figure S7. ^{13}C NMR spectrum (125 MHz, CD_3CN , 22 °C) of rotaxane **5**.

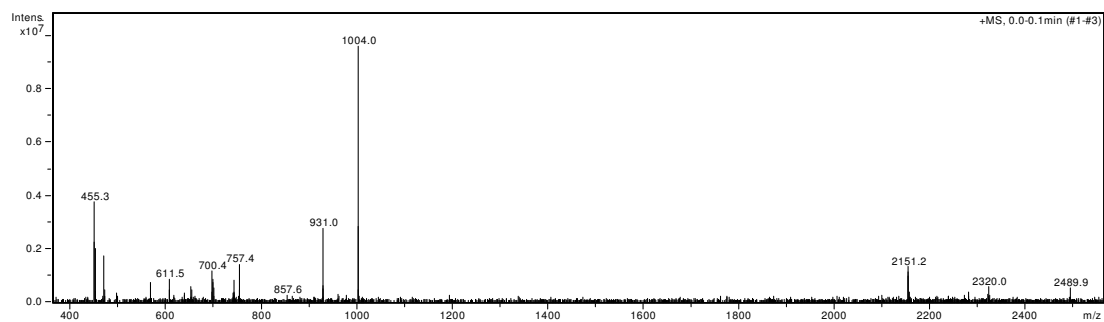


Figure S8. Low-resolution ESI-MS spectrum of rotaxane **5**.

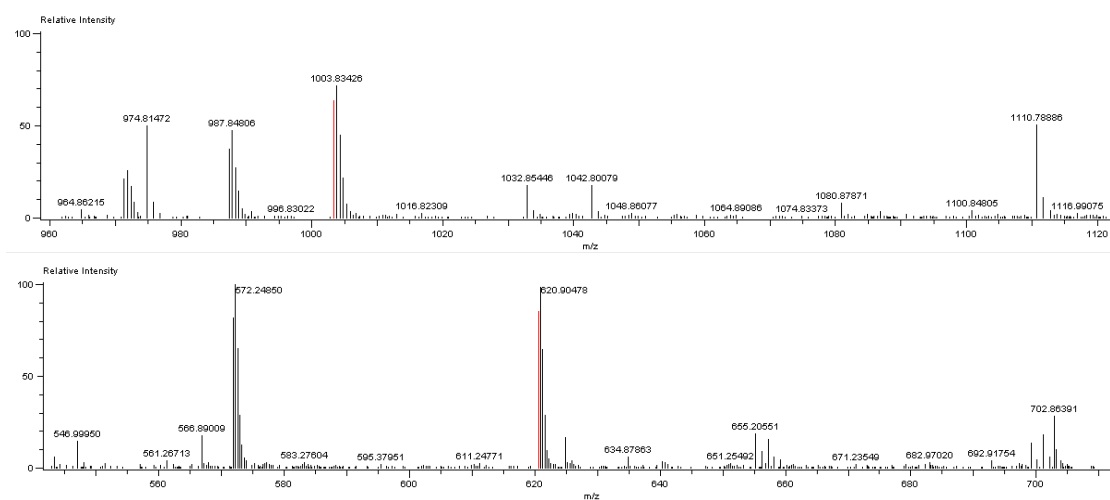
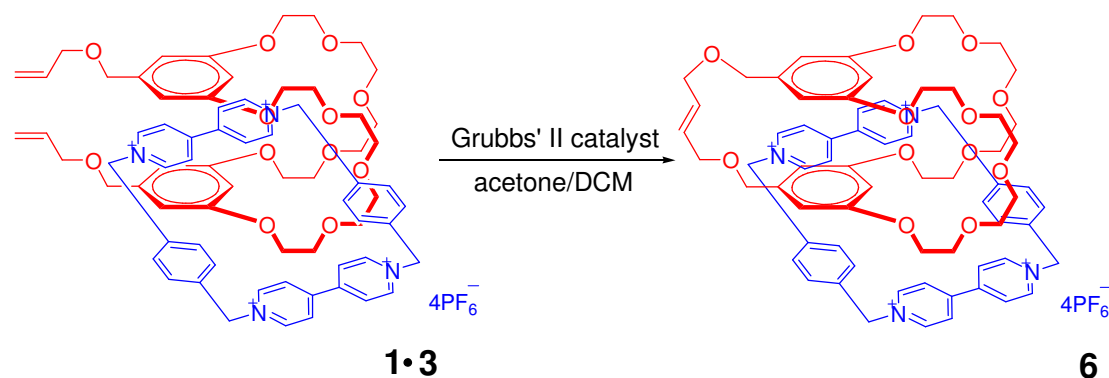


Figure S9. High-resolution ESI-MS spectrum of rotaxane **5**.

5. Synthesis and characterization of [2]catenane **6**



BMP32C10 derivative **1** (20.0 mg, 0.0284 mmol) and cyclophane **3** (26.0 mg, 0.0236 mmol) was dissolved in acetone (20 mL) under nitrogen atmosphere. Then a solution of Grubbs' II catalyst (2.00 mg) in DCM (4 mL) was added at room temperature. The mixture was then stirred for 24 h. The solvent was evaporated *in vacuo* and the residue was purified by column chromatography (SiO₂: MeOH/NH₄Cl (2 M)/MeNO₂ = 17:2:1) to afford [2]catenane **6** (35.1 mg, 85%) as a yellow solid, mp 275–276 °C. ¹H NMR (500 MHz, CD₃CN, 22 °C) δ (ppm): 8.93 (8 H, br), 7.70 (16 H, br), 6.10 (2 H, br), 5.74 (10 H, br), and 4.08–3.62 (44 H, m). ¹H NMR (125 MHz, CD₃CN, 22 °C) δ (ppm): 159.8, 145.8, 137.0, 131.6, 127.0, 126.4, 71.8, 71.4, 70.5, 70.2, 68.4, and 65.7. Low-resolution ESI-MS: m/z 1605.6 (75%) [**6** – PF₆ + H]⁺, and 729.8 (100%) [**6** – 2PF₆]²⁺. High-resolution ESIMS: m/z calcd for [**6** – 2PF₆]²⁺ C₇₀H₈₀F₁₂N₄O₁₂P₂, 729.2528, found 729.2542, error 1.9 ppm.

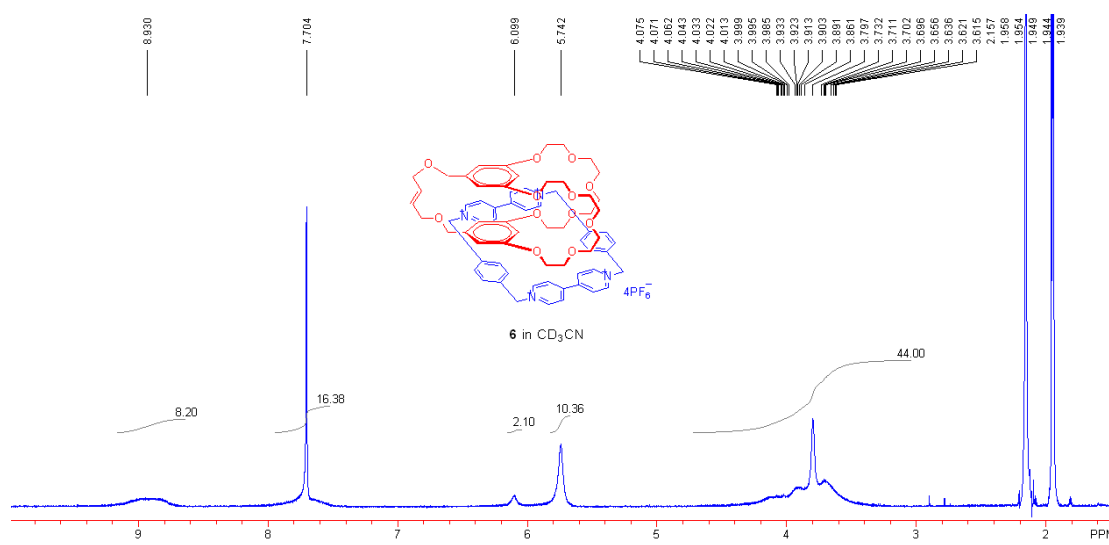


Figure S10. ¹H NMR spectrum (500 MHz, CD₃CN, 22 °C) of catenane **6**.

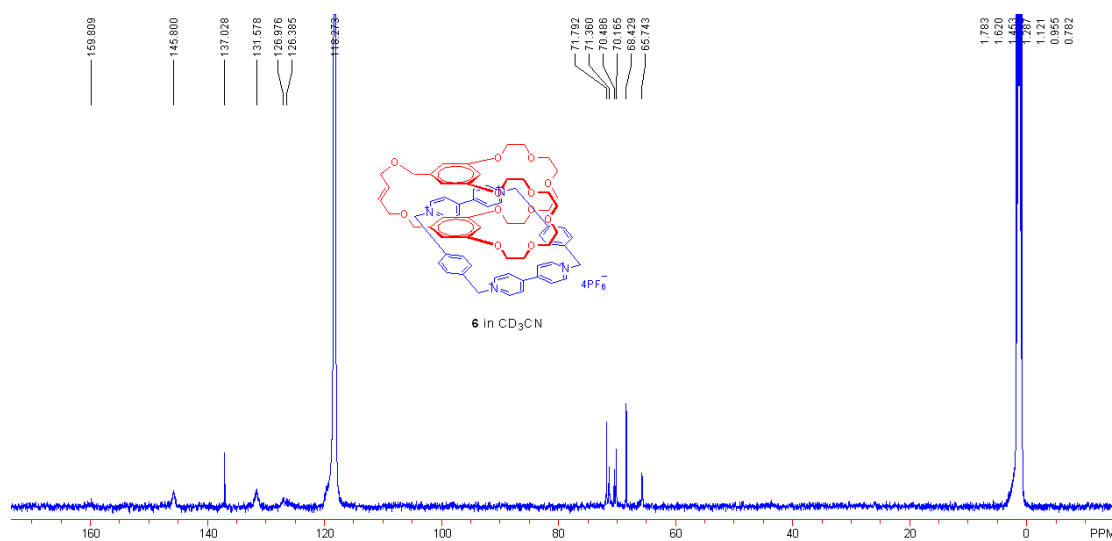


Figure S11. ¹³C NMR spectrum (125 MHz, CD₃CN, 22 °C) of catenane **6**.

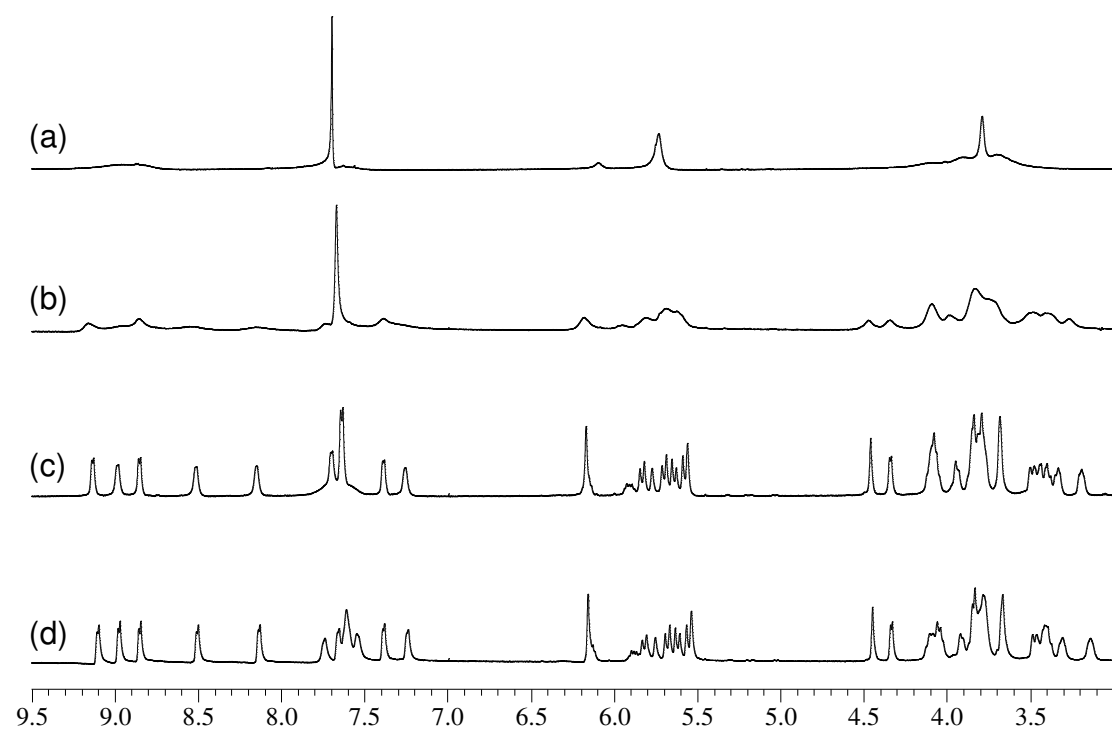


Figure S12. The partial temperature-dependent ¹H NMR spectra (125 MHz, CD₃CN) of catenane **6** at 25 °C (a), 0 °C (b), -20 °C (c), and -40 °C (d).

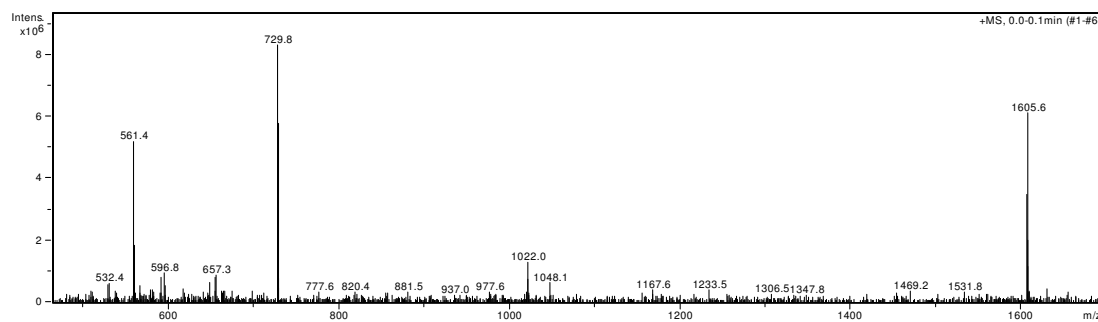


Figure S13. Low-resolution ESI-MS spectrum of catenane **6**.

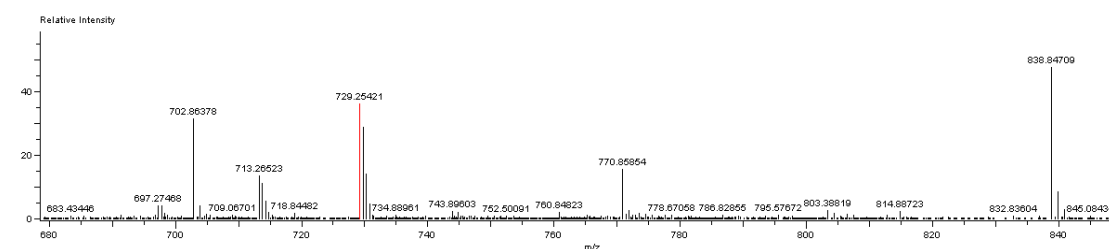


Figure S14. High-resolution ESI-MS spectrum of catenane **6**.

6. UV-Vis absorption spectra of the dumbbell-shaped paraquat derivative **2**, cyclophane **3**, cryptand **4**, rotaxane **5**, and catenane **6**

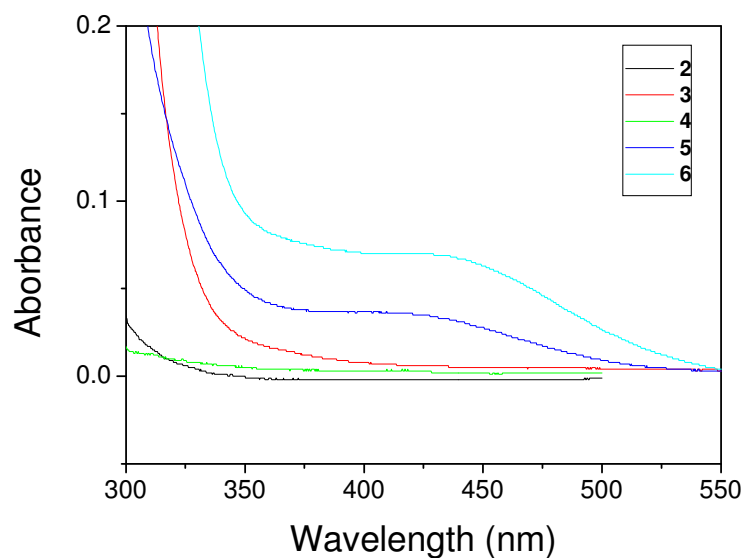


Figure S15. The UV-Vis absorption spectra of the dumbbell-shaped paraquat derivative **2**, cyclophane **3**, cryptand **4**, rotaxane **5**, and catenane **6** at a concentration of 0.1 mM in acetonitrile.

7. X-ray analysis data of BMP32C10 derivative **1**

Crystallographic data: block, colorless, $0.652 \times 0.426 \times 0.229 \text{ mm}^3$, $\text{C}_{36}\text{H}_{52}\text{O}_{12}$, FW 676.79, triclinic, space group P^{-1} , $a = 7.0217(2)$, $b = 11.5023(4)$, $c = 12.3086(4) \text{ \AA}$, $\alpha = 113.4510(10)^\circ$, $\beta = 94.5990(10)^\circ$, $\gamma = 97.8820(10)^\circ$, $V = 893.40(5) \text{ \AA}^3$, $Z = 2$, $D_c = 1.258 \text{ g cm}^{-3}$, $T = 173(2) \text{ K}$, $\mu = 0.094 \text{ mm}^{-1}$, 10340 measured reflections, 3124 independent reflections, 229 parameters, 0 restraints, $F(000) = 364$, $R_1 = 0.0360$, $wR_2 = 0.0932$ (all data), $R_1 = 0.0338$, $wR_2 = 0.0908$ [$I > 2\sigma(I)$], max. residual density $0.167 \text{ e}\cdot\text{\AA}^{-3}$, and goodness-of-fit (F^2) = 1.052.

8. X-ray analysis data of [2]catenane **6**

Crystallographic data: block, orange, $0.529 \times 0.220 \times 0.084 \text{ mm}^3$, $\text{C}_{70}\text{H}_{79}\text{F}_{24}\text{N}_4\text{O}_{12}\text{P}_4$, FW 1748.25, triclinic, space group P^{-1} , $a = 13.3566(7)$, $b = 13.8761(7)$, $c = 26.4176(13) \text{ \AA}$, $\alpha = 77.624(2)^\circ$, $\beta = 84.730(2)^\circ$, $\gamma = 78.959(2)^\circ$, $V = 4687.3(4) \text{ \AA}^3$, $Z = 2$, $D_c = 1.239 \text{ g cm}^{-3}$, $T = 173(2) \text{ K}$, $\mu = 0.179 \text{ mm}^{-1}$, 54027 measured reflections, 16311 independent reflections, 1036 parameters, 0 restraints, $F(000) = 1798$, $R_1 = 0.1395$, $wR_2 = 0.3084$ (all data), $R_1 = 0.1030$, $wR_2 = 0.2814$ [$I > 2\sigma(I)$], max. residual density $1.828 \text{ e}\cdot\text{\AA}^{-3}$, and goodness-of-fit (F^2) = 0.978.

References:

S1. Gibson, H. W.; Nagvekar, D. S. *Can. J. Chem.* **1997**, 75, 1375–1384.